

Coherent X-ray Scattering and X-ray Photon Correlation Spectroscopy

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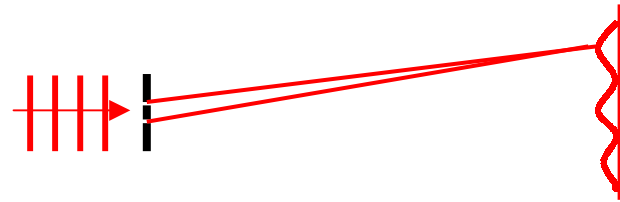
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What is Coherence?

Ideal Young's double slit experiment

Intensity varies as

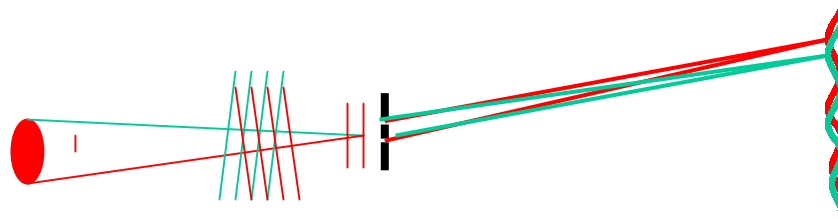
$$I = 2I \left[1 + \cos \left(2\pi d \sin(\theta) / \lambda \right) \right]$$



Real Young's double slit experiment

Intensity varies as

$$I = 2I \left[1 + \beta \cos \left(2\pi d \sin(\theta) / \lambda \right) \right]$$



β is the contrast, determined by the angular size of the source

Coherence Length and Contrast

It is generally convenient to assume the source has a Gaussian intensity profile

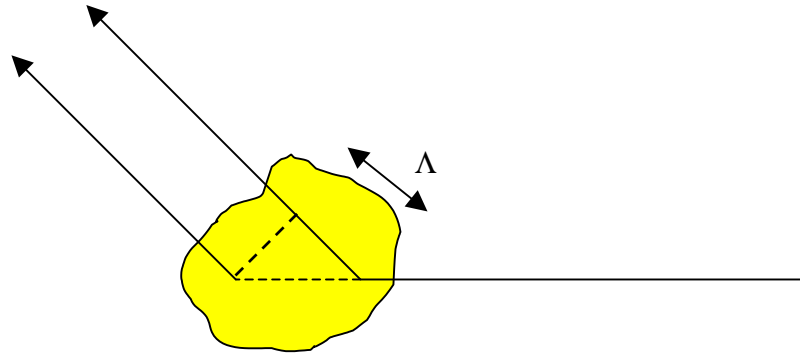
$$I(x) = \frac{I_0}{\sqrt{2\pi}\xi} \exp\left[-(x - x_0)^2 / 2\sigma^2\right]$$

One can then define a coherence length

$$\xi = \frac{\lambda R}{2\sigma\sqrt{\pi}}$$

This characterizes the distance over which two slits would produce an interference pattern, or more generally the length scale over which any sample will produce interference effects.

Longitudinal coherence



$$\Lambda \approx \lambda(E / \Delta E)$$

e.g. the number of wavelengths that can be added before the uncertainty adds up to a full wavelength.

How Practical is it to Make X-rays Coherent?

Consider a point 65 meters downstream of an APS

Undulator A $\lambda = 0.2\text{nm}, \quad \Delta\lambda/\lambda = 3 \times 10^{-4}$

$$\sigma_x = 254\mu\text{m}, \sigma_y = 12$$

$$\xi_x = \frac{\lambda R}{2\sigma_x \sqrt{\pi}} = 14\mu\text{m}$$

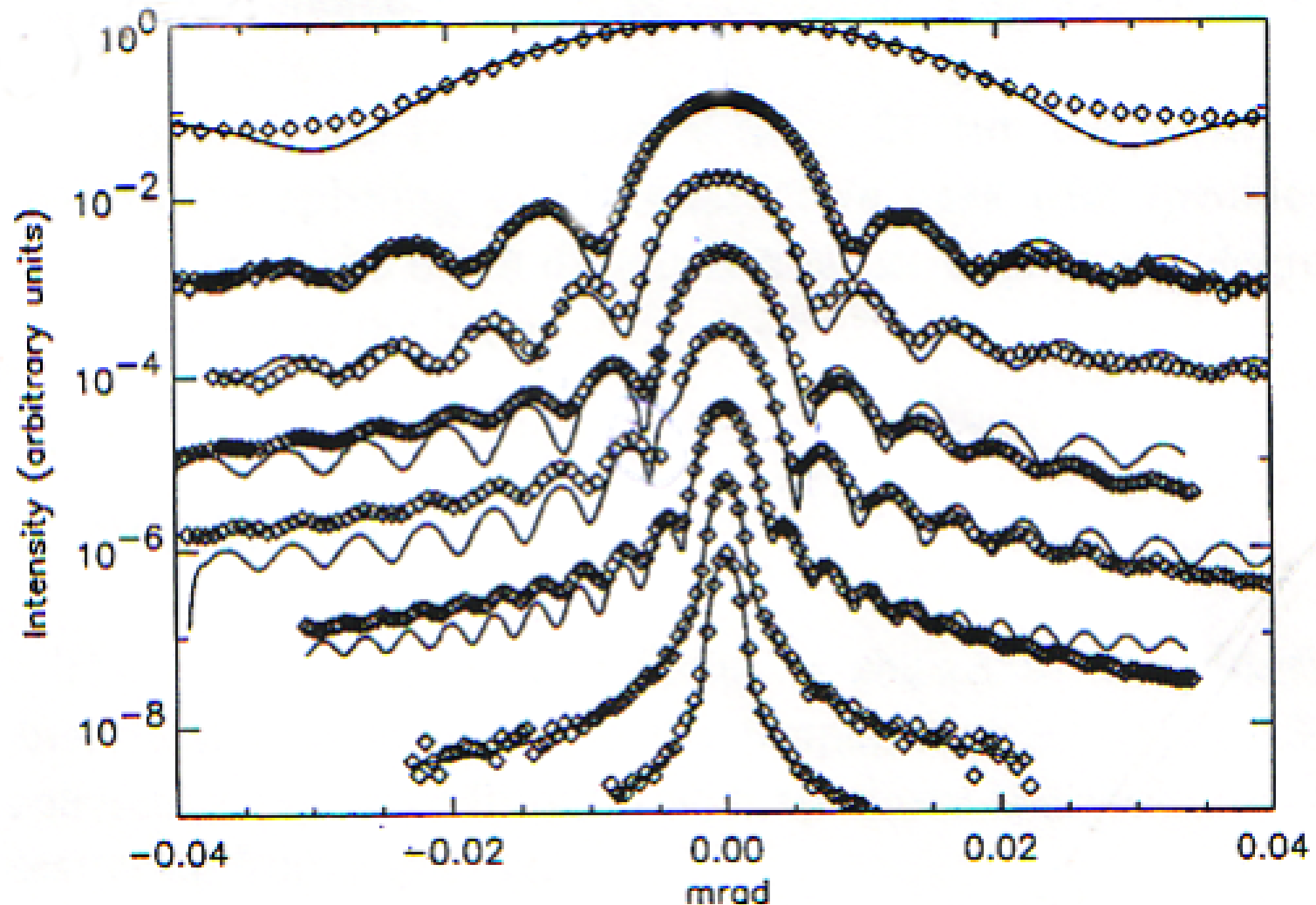
$$\xi_y = \frac{\lambda R}{2\sigma_y \sqrt{\pi}} = 306\mu\text{m}$$

$$\Lambda = 67\mu\text{m}$$

$$\sim 3 \times 10^{10} \text{ Photons/Coherence Area}$$

Fraunhofer X-ray Diffraction from a Slit

B. Lin et. al. RSI 67, (9) (1996)



Scattering of Coherent X-rays

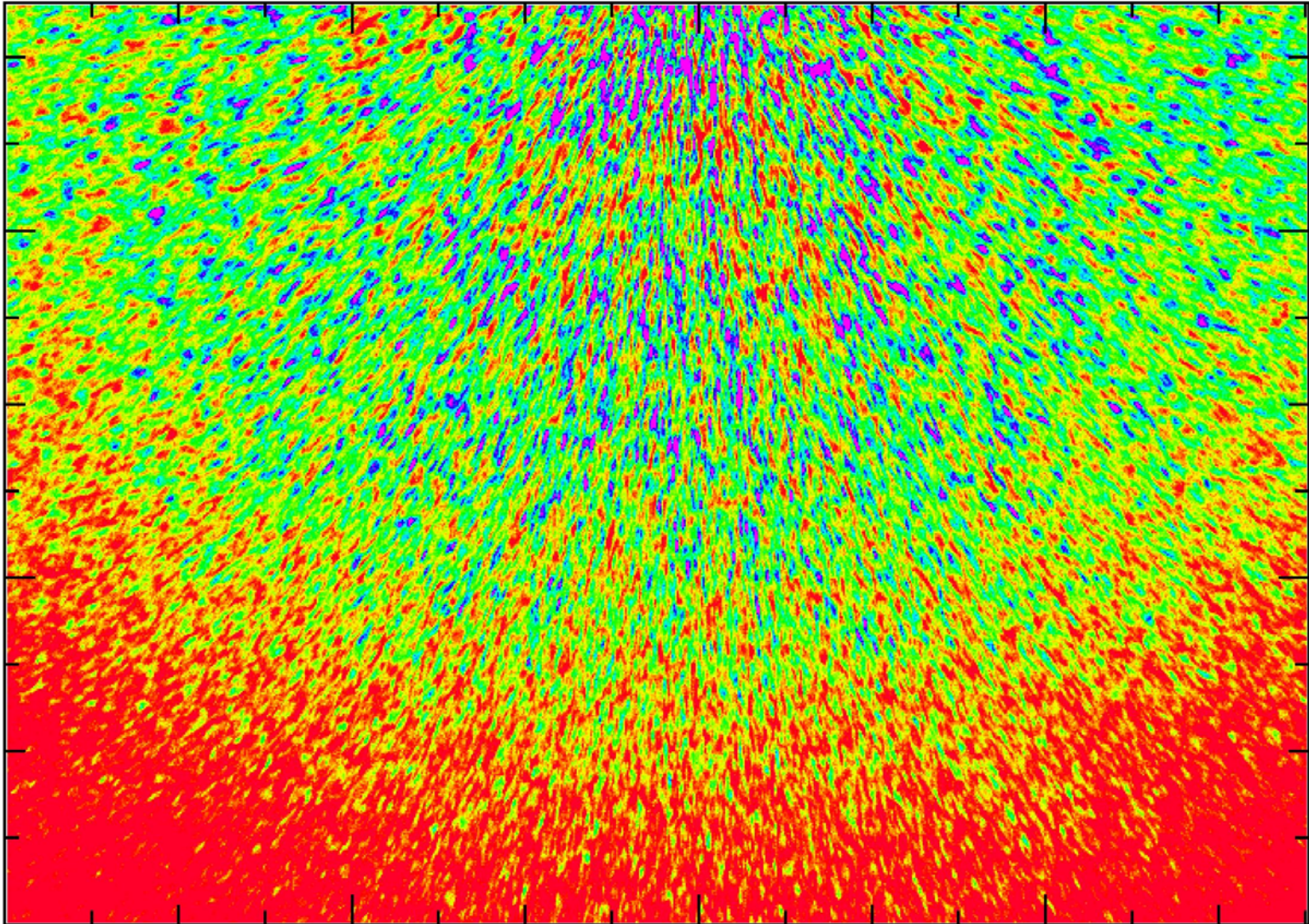
$$I(Q) \sim \int \int e^{i\vec{Q} \cdot \vec{r}''} \rho_e(\vec{r}) \rho_e(\vec{r} - \vec{r}'') d\vec{r} d\vec{r}''$$

For incoherent x-rays the actual scattering represents a statistical average over many incoherent regions within the sample and one obtains:

$$\rho_e(\vec{r}) \rho_e(\vec{r} - \vec{r}'') \approx \left\langle \rho_e(\vec{r}) \rho_e(\vec{r} - \vec{r}'') \right\rangle \equiv g(\vec{r})$$

For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.

Coherent Scattering from a Silica Aerogel

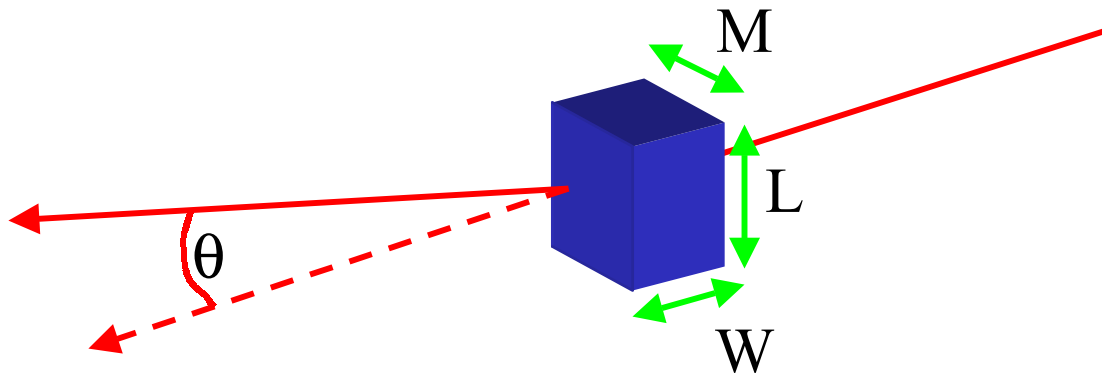


Speckle Size and Contrast

The average angular size of the speckles is, approximately, given by the diffraction limit of the illuminated sample area:

$$\Delta\theta \sim \lambda / L$$

The contrast is given by the ratio of the scattering volume $V_s \approx MLW \sin(\theta)$ to the coherence volume $\Lambda_{\xi_x \xi_y}$

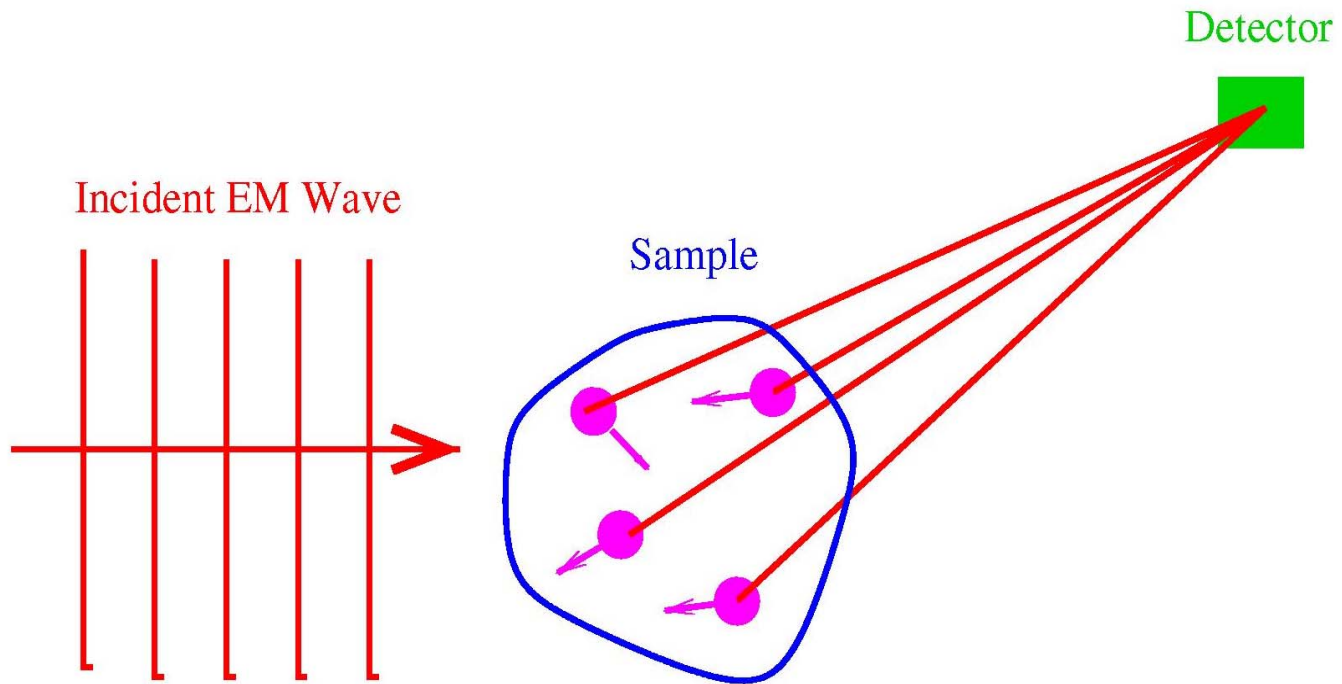


This is just an estimate and exact numbers require integrals over the sample volume and electric field spatial correlation function. Note also, that for small angles, the scattering volume is much smaller than the sample volume.

What to do with coherent x-rays?

- Try to invert the speckle to get information about the exact structure factor. (e.g I. K. Robinson et. al., PRL, 87, 195505)
- Ignore the details of the exact structure factor, but use the time fluctuations of the pattern to study dynamics of the material (XPCS)

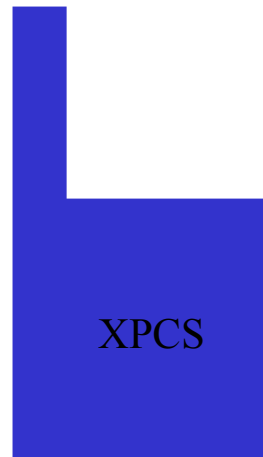
Measuring Dynamics



Typical applications are where the average structure is constant, but the local structure fluctuates.

- Diffusion of particles in solution
- Diffusion in polymer blends
- Motion of domain walls in a crystal
- Fluctuations in density within a binary fluid near its phase separation point.
- Thermally driven surface height fluctuations in a viscous fluid

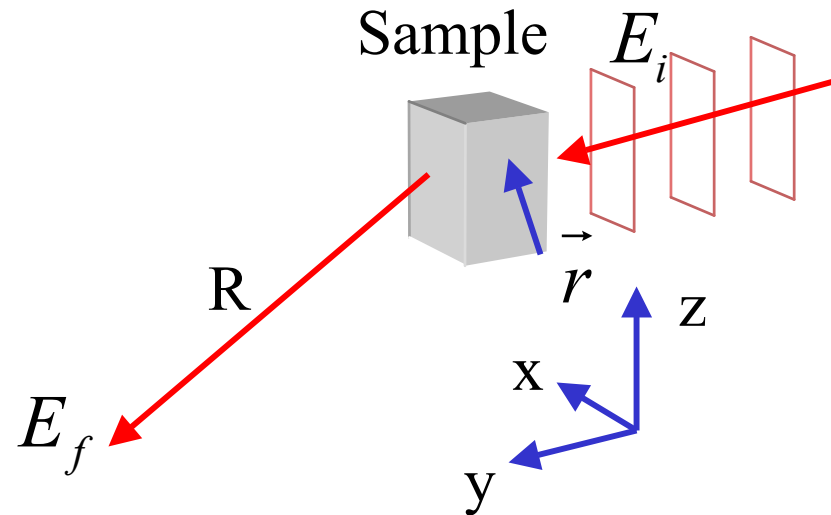
Phase space for XPCS



Why XPCS rather than PCS?

- Can measure smaller length scales
- Can measure structures associated with crystalline or semi-crystalline order
- Can measure opaque samples
- Multiple scattering not a serious problem
- Stray scattering much less of a problem

The Intensity-Intensity Correlation Function



$$E_f(t') = \frac{\hat{e}_f (\hat{e}_f \cdot \hat{e}_i) r_0 e^{i\omega t}}{R} \int d\vec{r} e^{i\vec{Q} \cdot \vec{r}} \rho_e(\vec{r}, t) E_i\left(\vec{r}, t - \frac{\vec{k}_f \cdot \vec{r}}{\omega}\right)$$

$$= \frac{\hat{e}_f (\hat{e}_f \cdot \hat{e}_i) r_0 e^{i\omega t}}{R} \int d\vec{r} e^{i\vec{Q} \cdot \vec{r}} \rho_e(\vec{r}, t) E_i\left(x, 0, z, t - \frac{\vec{Q} \cdot \vec{r}}{\omega}\right)$$

$$\vec{Q} = \vec{k}_f - \vec{k}_i, t' = t + R/c$$

Intensity Intensity Correlation Function (2)

We want the intensity intensity correlation function, given by:

$$\left\langle I(\vec{R} + \vec{\delta R}_1, t) I(\vec{R} + \vec{\delta R}_2, t + \tau) \right\rangle \quad \text{Let} \quad \vec{s}_{1,2} = k_f \frac{\vec{\delta R}_{1,2}}{R}$$

$$= \frac{V(\hat{e}_f \cdot \hat{e}_i)^4 r_0^4}{R^4} \iiint \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \exp\left(-i\left((\vec{Q} + \vec{s}_1) \cdot (\vec{r}_1 - \vec{r}_2) + (\vec{Q} + \vec{s}_2) \cdot (\vec{r}_3 - \vec{r}_4)\right)\right)$$

$$\left\langle \rho_e(\vec{r}_1, t) \rho_e(\vec{r}_2, t) \rho_e(\vec{r}_3, t + \tau) \rho_e(\vec{r}_4, t + \tau) \right\rangle$$

$$\left\langle E_i \left(x_1, 0, z_1, t - \frac{(\vec{Q} + \vec{s}_1) \cdot \vec{r}_1}{\omega} \right) E_i^* \left(x_2, 0, z_2, t - \frac{(\vec{Q} + \vec{s}_2) \cdot \vec{r}_2}{\omega} \right) \right.$$

$$\left. E_i \left(x_3, 0, z_3, t + \tau - \frac{(\vec{Q} + \vec{s}_1) \cdot \vec{r}_3}{\omega} \right) E_i^* \left(x_4, 0, z_4, t + \tau - \frac{(\vec{Q} + \vec{s}_2) \cdot \vec{r}_4}{\omega} \right) \right\rangle$$

This can be reduced to products of the pair correlation functions!

$$\begin{aligned}
 \left\langle I(\vec{R} + \vec{\delta R}_1, t) I(\vec{R} + \vec{\delta R}_2, t + \tau) \right\rangle &= \langle I \rangle^2 + \frac{(\hat{e}_f \cdot \hat{e}_i)^4 r_0^4}{R^4} \langle |E_i|^2 \rangle \int d\vec{r} e^{i\vec{Q} \cdot \vec{r}} \left\langle \rho_e(0, 0) \rho_e(\vec{r}, t) \right\rangle \\
 &\int \int d\vec{r}_1 d\vec{r}_2 e^{i(\vec{s}_2 - \vec{s}_1) \cdot (\vec{r}_2 - \vec{r}_1)} \left\langle E_i(x_1, 0, z_1, -\vec{Q} \cdot \vec{r}_1 / \omega) E_i^*(x_2, 0, z_2, -\vec{Q} \cdot \vec{r}_2 / \omega) \right\rangle \\
 &\equiv G_2(\vec{\delta R} - \vec{\delta R}, \tau)
 \end{aligned}$$

Important assumptions:

- Correlation lengths are much smaller than the sample size
- Radiation has cross-spectral purity (factors into a time and a space part)

Define the normalized correlation function

$$g_2(\vec{r}, \tau) \equiv G_2(\vec{r}, \tau) / \langle I \rangle^2$$

Time Autocorrelation of a Speckle Intensity

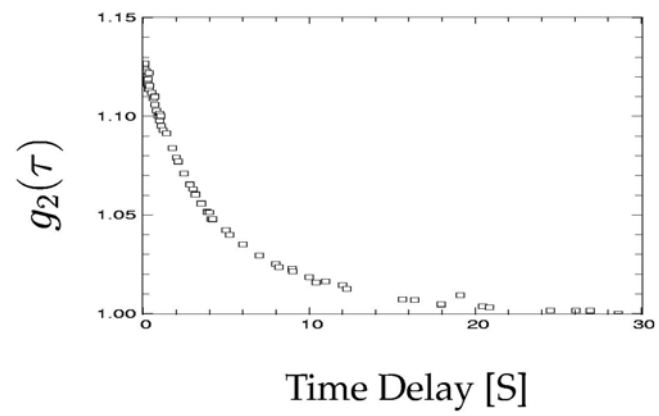
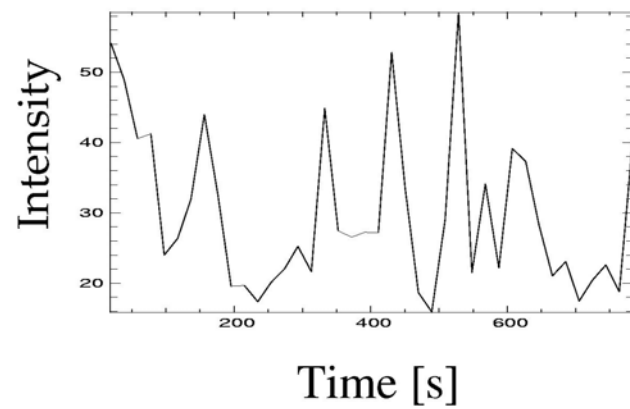
$$g_2(\tau) = 1 + \beta f(Q, \tau)^2$$

with

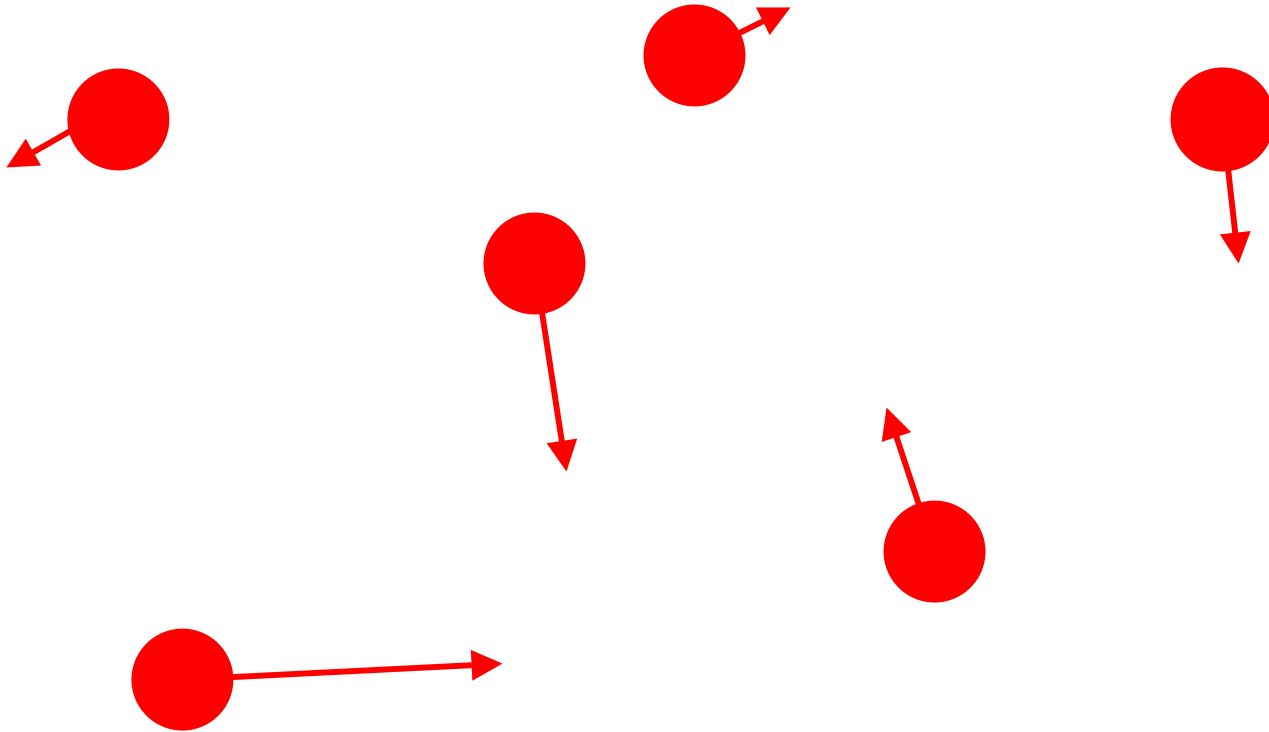
$$f(\vec{Q}, \tau) = S(\vec{Q}, \tau) / S(\vec{Q}, 0)$$

$$S(\vec{Q}, \tau) = \left\langle \int e^{i\vec{Q} \cdot \vec{r}} \rho_e(0, 0) \rho_e(\vec{r}, \tau) d\vec{r} \right\rangle$$

And β (the contrast) the integral of the red term over the detector acceptance (varies from 0 to 1).



A dilute colloidal solution



$$f(\vec{Q}, \tau) = \frac{1}{N} \sum_{i,j} \left\langle \exp(i\vec{Q} \cdot (\vec{r}_i(t) - \vec{r}_j(t + \tau))) \right\rangle$$

$$\approx \frac{1}{N} \sum_i \left\langle \exp(i\vec{Q} \cdot (\vec{r}_i(t) - \vec{r}_i(t + \tau))) \right\rangle$$

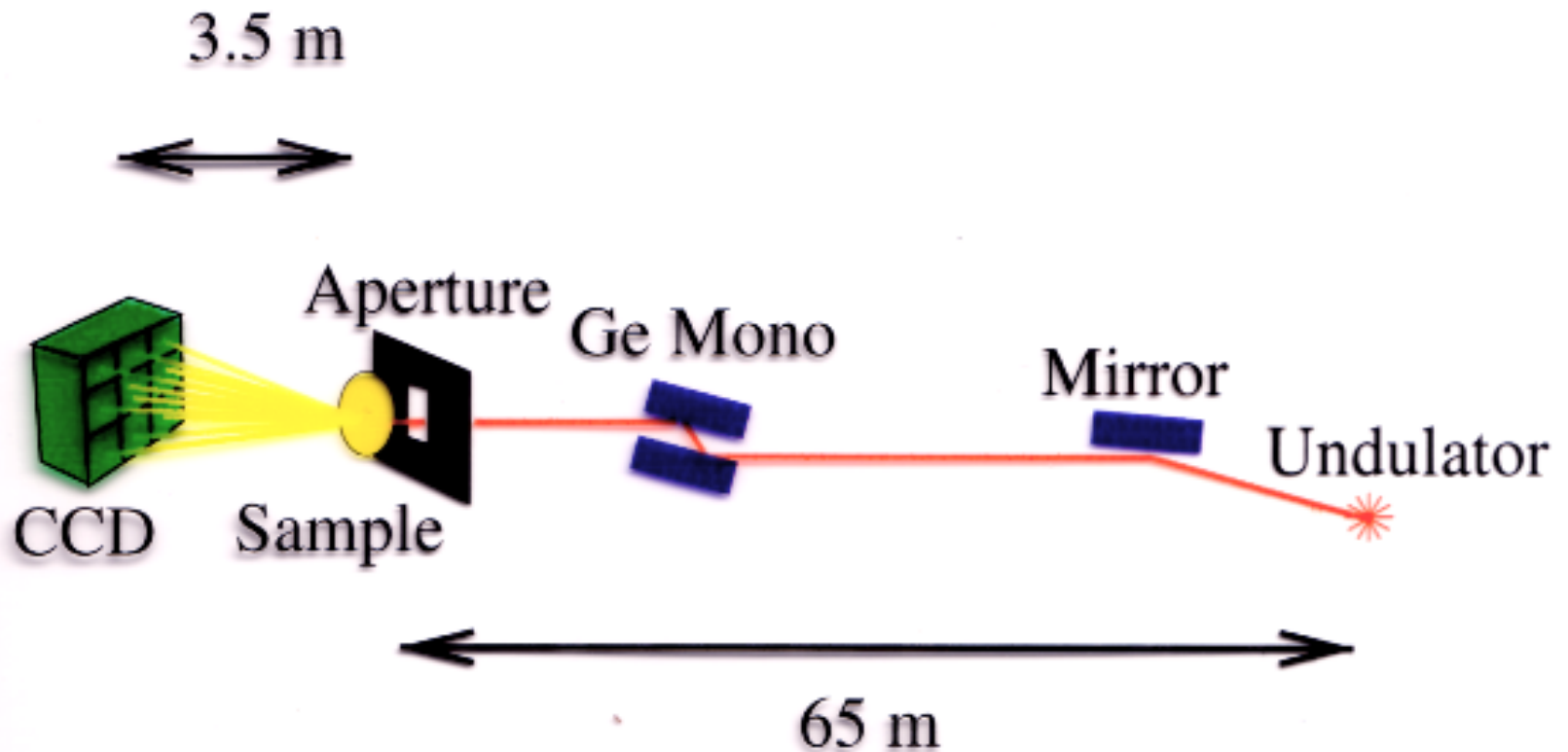
$$= \exp \left(\frac{Q^2 \left\langle \vec{r}_i(t) - \vec{r}_i(t + \tau) \right\rangle^2}{2} \right)$$

$$\left\langle \vec{r}_i(t) - \vec{r}_i(t + \tau) \right\rangle^2 = 2D\tau$$

$$f(Q, \tau) = \exp(-DQ^2\tau) = \exp(-\Gamma\tau)$$

$$\Gamma = DQ^2 = k_B T Q^2 / 6\pi\eta a$$

Setup for XPCS at Sector 8 of the APS

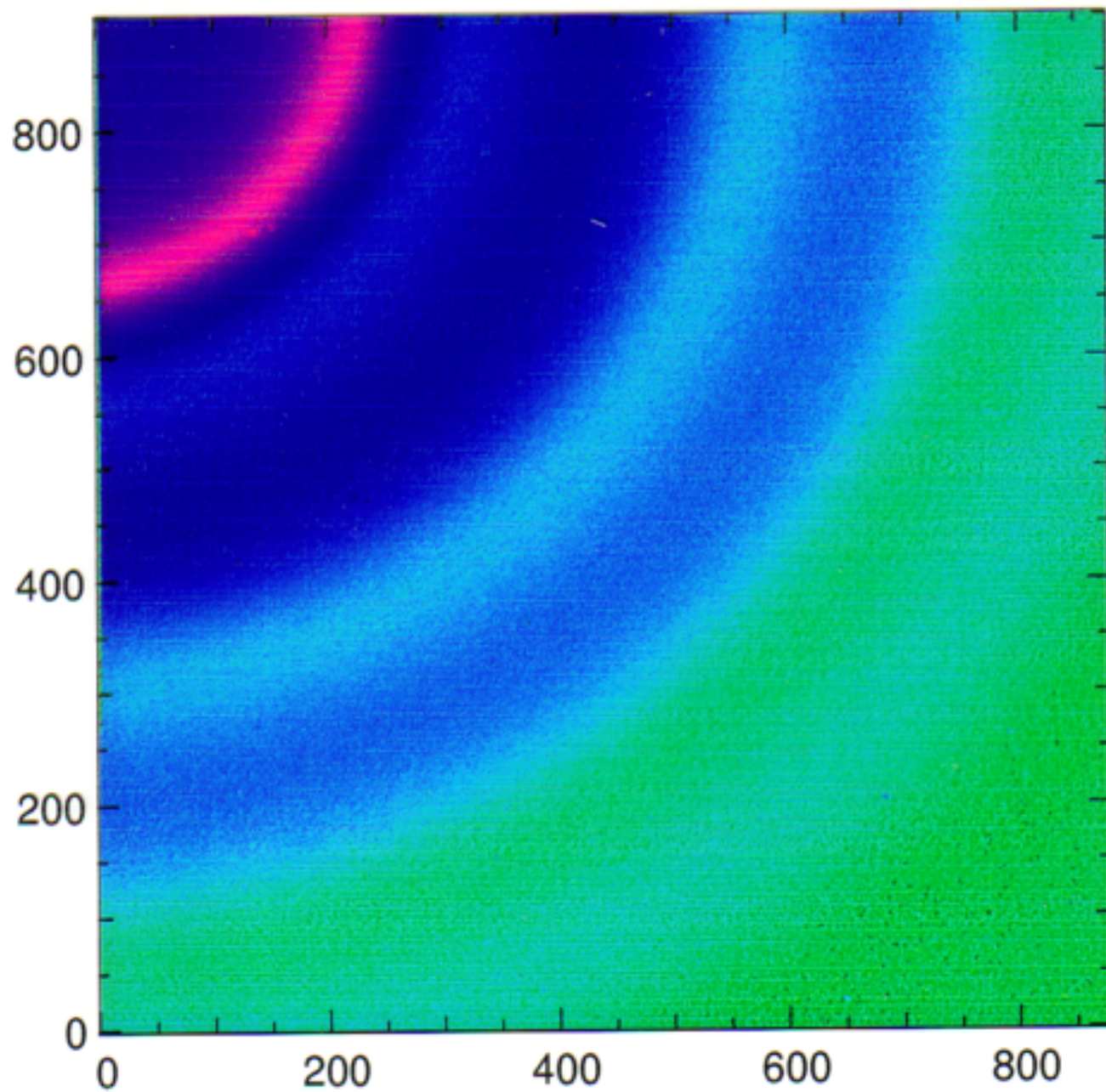


Dynamics of Colloidal Diffusion

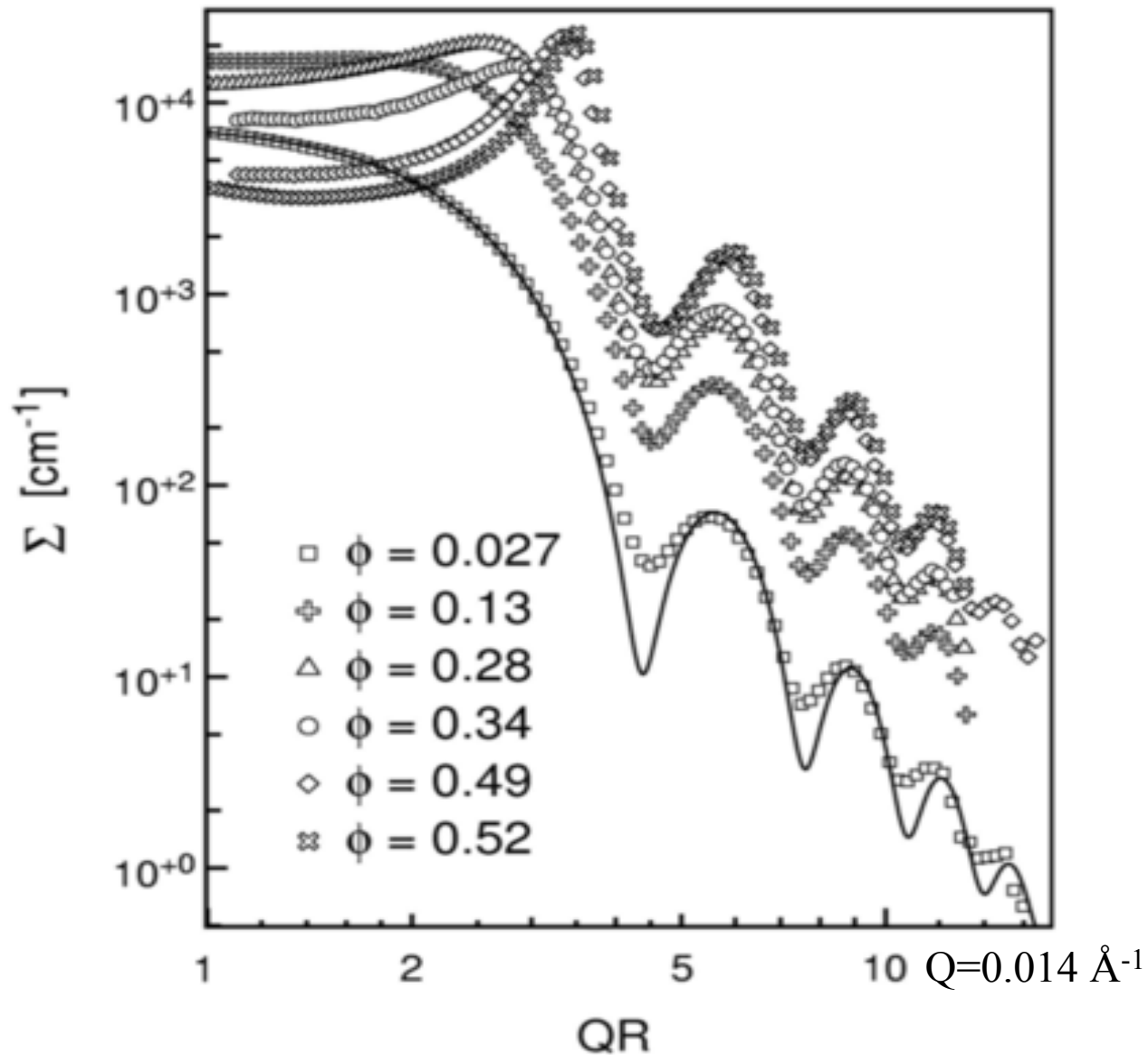
L. B. Lurio, D. Lumma, A. R. Sandy, M. A. Borthwick, P. Falus, and S. G. J. Mochrie J. F. Pelletier and M. Sutton Lynne Regan A. Malik and G. B. Stephenson PRL 84, 785 (2000)

- Charge stabilized suspension of polystyrene latex in glycerol
- 67 nm radius particles
- Volume fractions ranging from 2% to 57%
- Technological Relevance
 - Paints, Inks, Foods, Cosmetics
 - Protein crystallization
 - Self assembled nano-structures

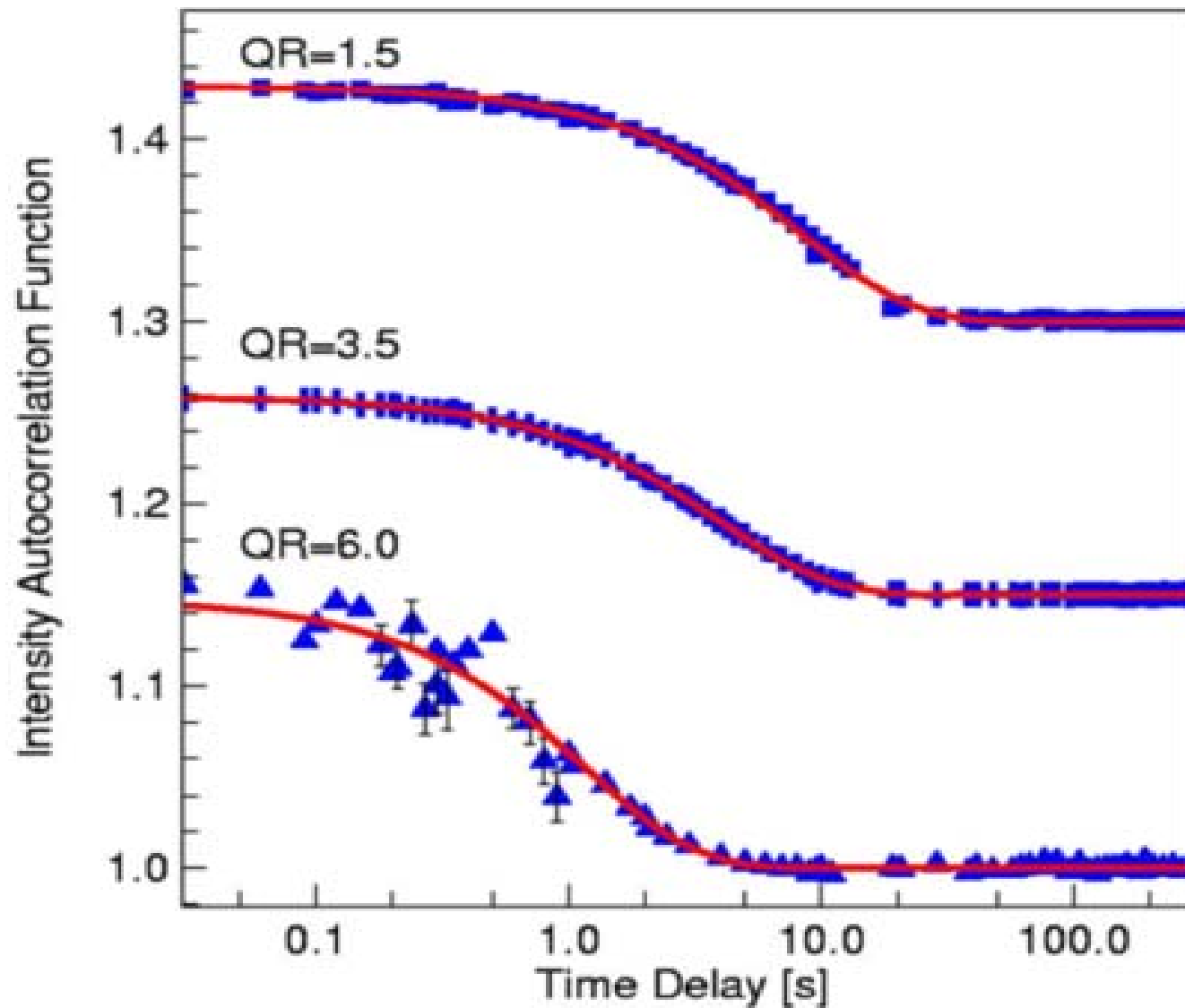
CCD Image: PS Latex in Glycerol [$\Phi = 0.49$]



Static Structure



Dynamics



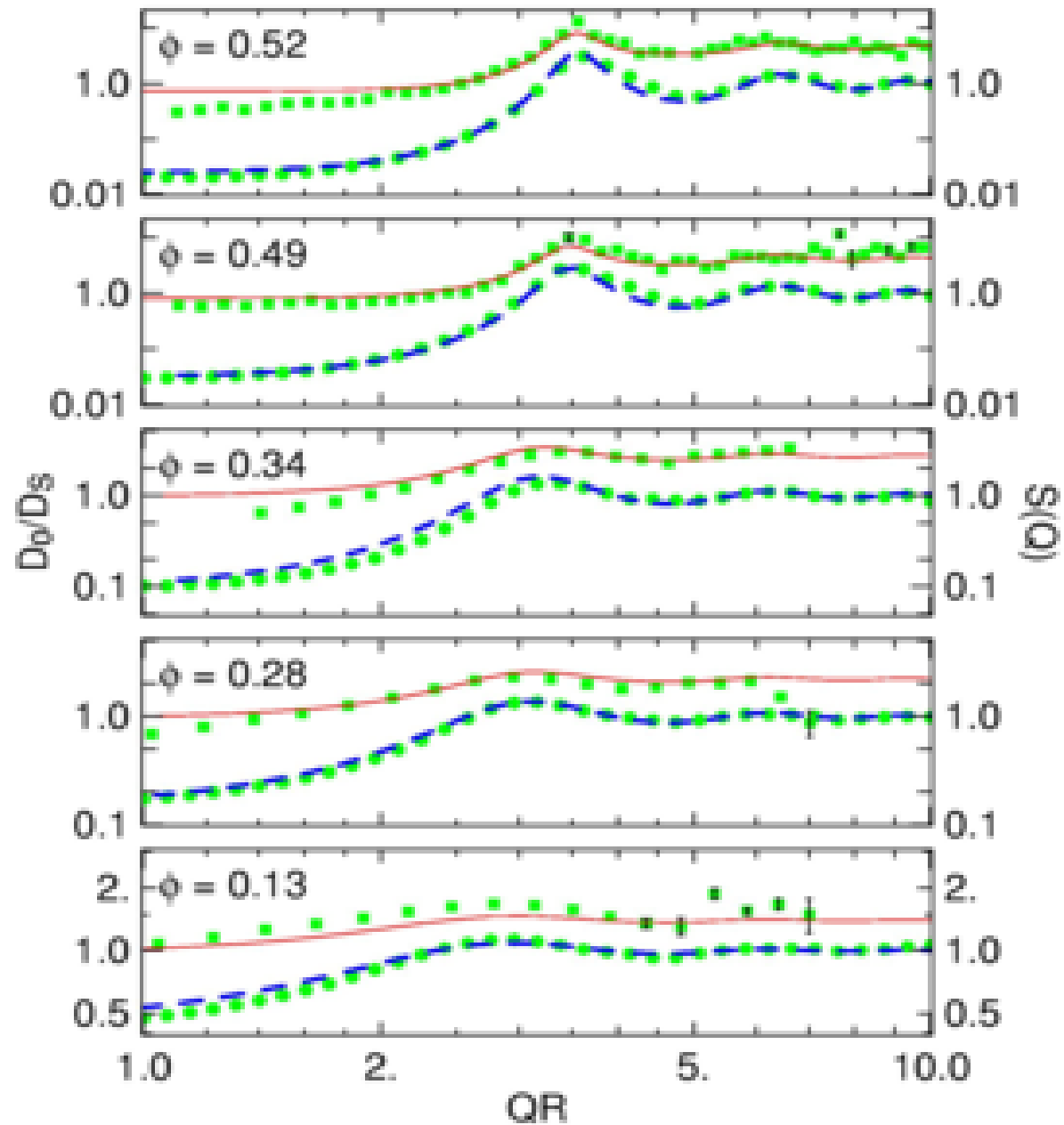
What about concentrated suspensions?

Two modifications to Brownian dynamics

1. Structural correlations lead to a slowing down of dynamics
2. Hydrodynamic interactions further modify the dynamics at high concentration
3. These effects can be calculated for the initial decay rate of the correlation function, but the $f(Q,t)$ will not generally be an exponential at long times.

$$D(Q) = D_0 H(Q) / S(Q)$$

Short Time Diffusion Constants

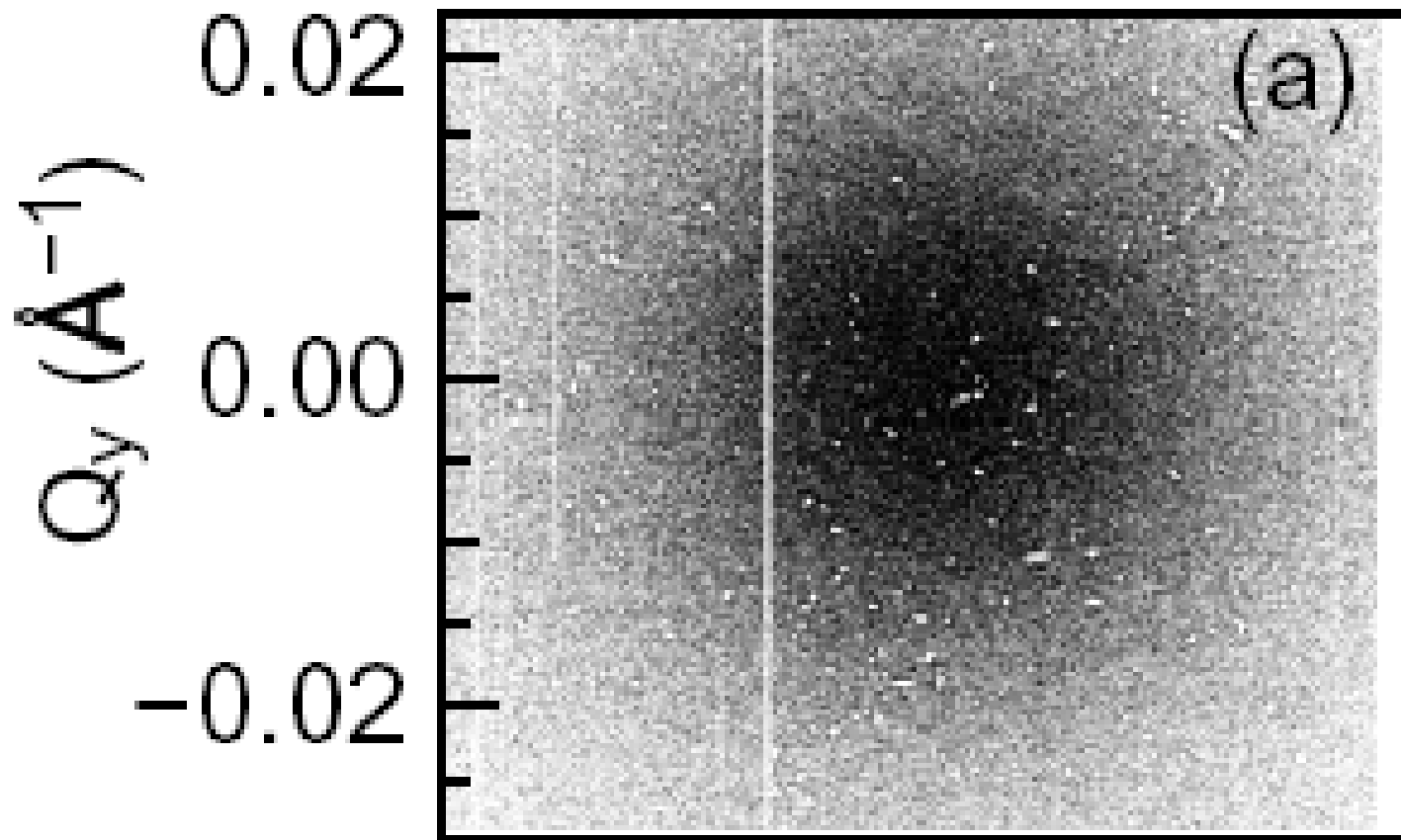


Equilibrium atomic fluctuations in Fe₃Al

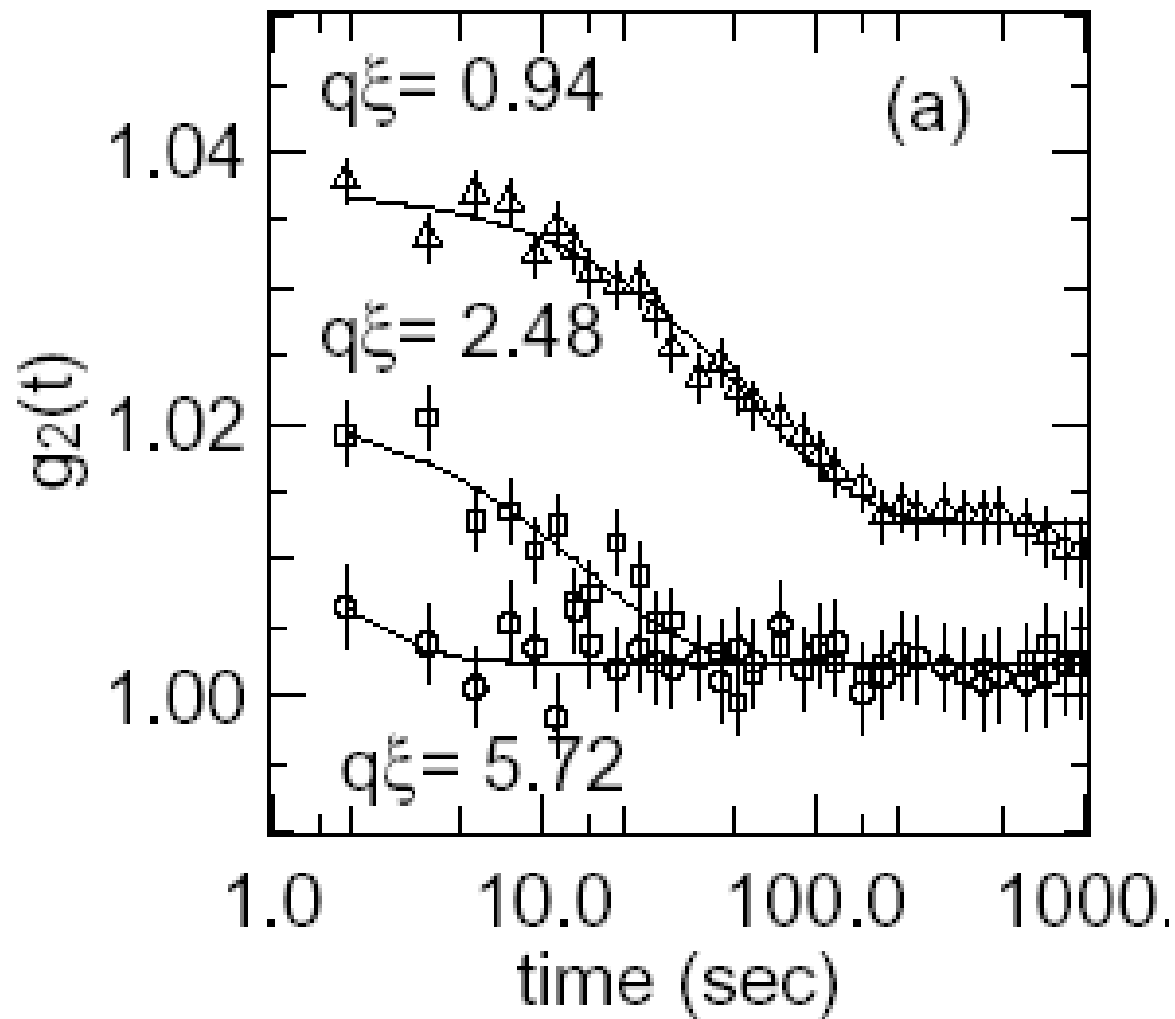
Khalid. Laaziri, M. Sutton, L.B. Lurio, A. Malik and G.B. Stephenson

- Look at scattering about a Bragg peak rather than small angle scattering
- Longitudinal coherence length is now important
- Two relevant length scales
- Use of Focusing Optics

Scattering around the Fe_3Al $(1/2, 1/2, 1/2)$ superlattice peak at 555C



Correlation Functions



Smectic Membranes in Motion: Approaching the Fast Limits of X-Ray Photon Correlation Spectroscopy

Irakli Sikharulidze,¹ Igor P. Dolbnya,² Andrea Fera,¹ Anders Madsen,³
Boris I. Ostrovskii,^{1,4} and Wim H. de Jeu¹

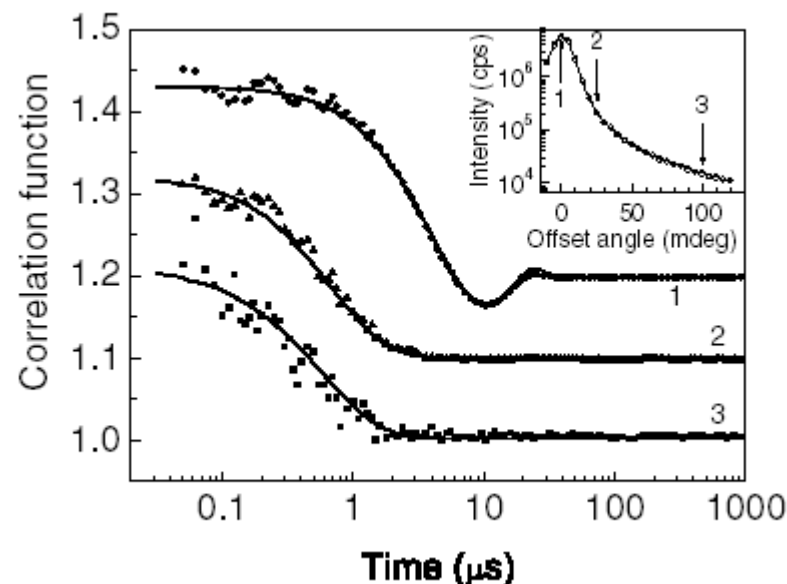
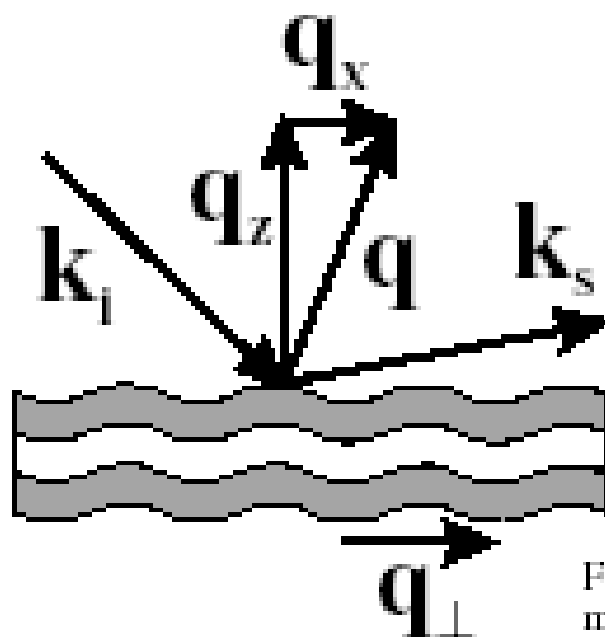


FIG. 3. Autocorrelation functions of a $2.83 \mu\text{m}$ thick FPP membrane at $q_z = 2.18 \text{ nm}^{-1}$ ($d = 2.94 \text{ nm}$). Circles show data at $q_x = 0$ (specular), triangles at an offset $q_x = 0.95 \times 10^{-3} \text{ nm}^{-1}$, and squares at $q_x = 3.8 \times 10^{-3} \text{ nm}^{-1}$. Solid lines are fits with parameters [14] $\gamma = 0.013 \text{ N/m}$, $\eta_3 = 0.015 \text{ kg m}^{-1} \text{ s}^{-1}$, $\rho_0 = 10^3 \text{ kg/m}^3$. Furthermore $\Delta q_x = 9 \times 10^{-5} \text{ nm}^{-1}$ and $\Lambda = 90 \mu\text{m}$. Curves 1 and 2 have been shifted by 0.1 and 0.2, respectively. Inset: rocking curve.